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Preparation of SiO_2-TiO_2 Gels with Controlled Pore Structure via Sol-Gel Route

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Gels in SiO_2-TiO_2 system with well-defined interconnected porous structure have been prepared by a polymer-incorporated sol-gel process based on a co-hydrolysis of silicon tetramethoxide and titanium tetrabutoxide. With an increase of TiO_2 content, the gelation time slightly decreased, and the size of the interconnected domains steeply decreased. The role of titanium alkoxide in the domain formation process was discussed in comparison to the effect of reaction temperature.

KEYWORDS : Sol-gel method / SiO_2-TiO_2 system / Organic polymer / Phase separation / Porous material

INTRODUCTION

Binary glasses in the system of SiO_2-TiO_2 with minor TiO_2 contents are known to exhibit a peculiar thermal expansion behavior[1]. In the temperature range between 25 and 700°C, the thermal expansion coefficient of pure SiO_2 glass is about 5×10^{-7} K^{-1}. With increasing TiO_2 content, it decreases and turns negative at around 6.5 mol% of TiO_2[1]. Glasses in this composition range can be used as transparent ultra-low expansion materials. Because of the high melting temperature of the above system, an alternative low-temperature process, a sol-gel method, has been proposed to prepare these glasses in the form of fiber, thin film or bulk[2,3].

On the other hand, we have reported a method to prepare pure silica gels with well-defined micrometer-range interconnected pores. An incorporation of a water-soluble organic polymer in the hydrolysis and polycondensation reactions of silicon alkoxides[4] enabled one to control the gel morphology in a broad range of length scales. When heat-treated at around 1000°C, the gels can be converted into SiO_2 glasses without losing their original porous morphology. The present study has aimed to extend this method to the system of SiO_2-TiO_2. Specifically, this paper concerns the role of added titanium alkoxide in the sol-gel reaction kinetics and morphology formation.

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EXPERIMENTAL

Silicon tetramethoxide (TMOS), purchased from Shin-Etsu Chemical Co., and titanium tetrabutoxide (TBOT), from Tokyo Chemical Industry Ltd., were used as SiO_2 and TiO_2 sources, respectively. Polyacrylic acid (HPAA) having an average molecular weight of 250,000 (PA25) from Aldrich Chemical Co., or that of 10,000 (PA1) synthesized by Toa Gosei Chemical Industry Co. Ltd. was used as a polymer component. All the other chemicals were in reagent grade, and used without further purification.

Sample gels were prepared by the following procedures; An appropriate amount of HPAA was dissolved in a given amount of distilled water and concentrated nitric acid was added. Then, a homogeneous mixture of TMOS and TBOT was added to this solution at 0°C under vigorous stirring. A hydrolysis reaction occurred in a few seconds accompanied by heat-evolution, and slightly yellowish transparent solution was obtained. Finally, the solution was poured into a polystyrene vessel, then tightly sealed, and kept at constant temperatures for gelation. The gelled sample was aged for few days, and was immersed in a large amount of $1mol \cdot dm^{-3}$ aqueous nitric acid solution for a few hours, then dried in an oven at 60°C.

The morphologies of dried gels were examined by a scanning electron microscope (SEM; S-510, Hitachi Co.) using flat fractured surfaces. Analyses of the pore structure were carried out on heat-treated gel samples by a mercury porosimetry (PORESIZER-9310, Micromeritics Corp.) and a nitrogen adsorption-desorption method (ASAP-2000, Micromeritics Corp.). The compositions of heat-treated gels were determined by an x-ray fluorescence analysis using precipitated amorphous SiO_2 and TiO_2 (anatase) as standards.

RESULTS AND DISCUSSION

(1) Preparation conditions

For pure SiO_2 systems, if appropriate starting compositions and reaction conditions are adopted, one can obtain gels with so-called interconnected structure which is composed of co-continuous oxide skeletons and pores[4]. The structure can be fixed as a permanent gel morphology only when a domain formation by a spinodal decomposition takes place concurrently with a sol-gel transition of the oxide component. The characteristic size of interconnected structure, often called "domain size", largely depends on the gel-forming rate of the oxide component and on mutual solubilities among the constituents. As either of these parameters increases, the spinodal decomposition is induced in later stages of the sol-gel reaction. This allows a domain formation to proceed in a "deeply quenched" state, and as a result, the domain size becomes small[4].

In order to extend the above process to SiO_2-TiO_2 system, a procedure based on a co-hydrolysis of TMOS-TBOT mixture was adopted. Under strongly acidic conditions, a limited part of added TBOT is expected to be chemically incorporated in the silicate gel network by forming Si-O-Ti bonds, and others will be stably dispersed as colloidal particles[5]. For more intimate mixing of the constituents, proposed is a partial pre-hydrolysis of less reactive silicon alkoxide followed by an addition of titanium alkoxide[6], or a slow *in situ* generation of water in the mixture of titanium and silicon alkoxides[7]. In the present case,

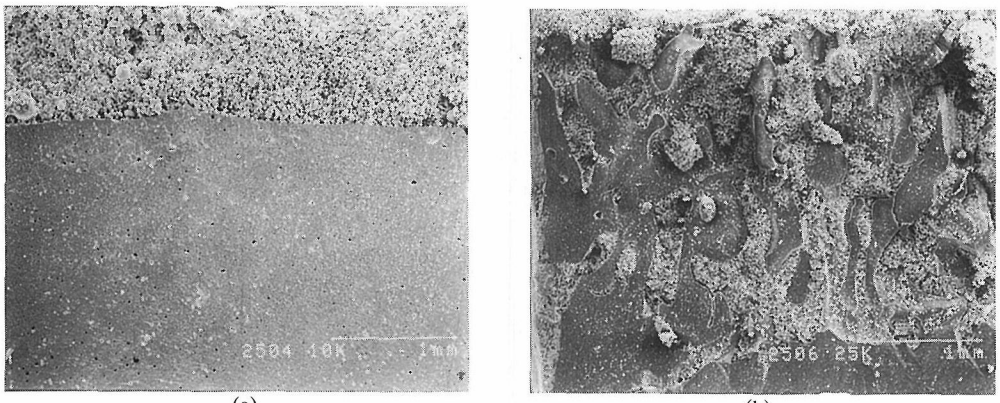
however, when TBOT was added to a solution containing pre-hydrolyzed TMOS and HPAA, gel-like insoluble precipitates were formed probably due to the formation of coordination bonds between carboxyl groups of HPAA and titanium atoms[8]. For these reasons, although the molecular level homogeneity might be reduced to some extent, the co-hydrolysis method was applied in a low TiO_2 concentration range up to 4.31 mol%.

(2) Effect of TBOT on gelation behavior and final morphology

Table 1 shows the representative starting compositions. In both PA1 and PA25 systems at 40°C, solutions prepared without TBOT formed gels after a complete liquid-phase separation into HPAA- and silica-rich phases, which gave a double-layered appearance (fig. 1(a)). Table 2 shows gelation times, t_g, of several samples containing PA25 as a polymer component. The amount of TBOT is expressed by m, the mole ratio of TBOT against the sum of TMOS and TBOT, which represents the mole fraction of TiO_2 in SiO_2-TiO_2 system. When the reaction temperature was raised to 60°C, the gelation time drastically decreased but still the solution became turbid before gelation. A quite coarse gel morphology was obtained showing an intermediate state from interconnected structure to macroscopic sedimentation (fig. 1(b)). This morphology indicates that the earlier stage of phase separation can be fixed at higher reaction temperature mainly by an accelerated gel formation[9]. By contrast, although the addition of TBOT reduced the gelation time only slightly, the sam-

Table 1. Starting compositions of SiO_2-TiO_2 gel samples. (unit:g)

Sample	HPAA		Water	60%HNO_3	TMOS	TBOT
ST25	PA25	0.40–0.48	10.0	1.0	9.13	0.798–0.913
ST1	PA1	1.42–2.13	10.0	1.0	9.13	0.913



(a) (b)

Fig. 1. SEM photographs of dried gels prepared from PA25-TMOS (S25) system. (a): 40°C, (b): 60°C.

Table 2 Starting composition and gelation time of several samples[a].

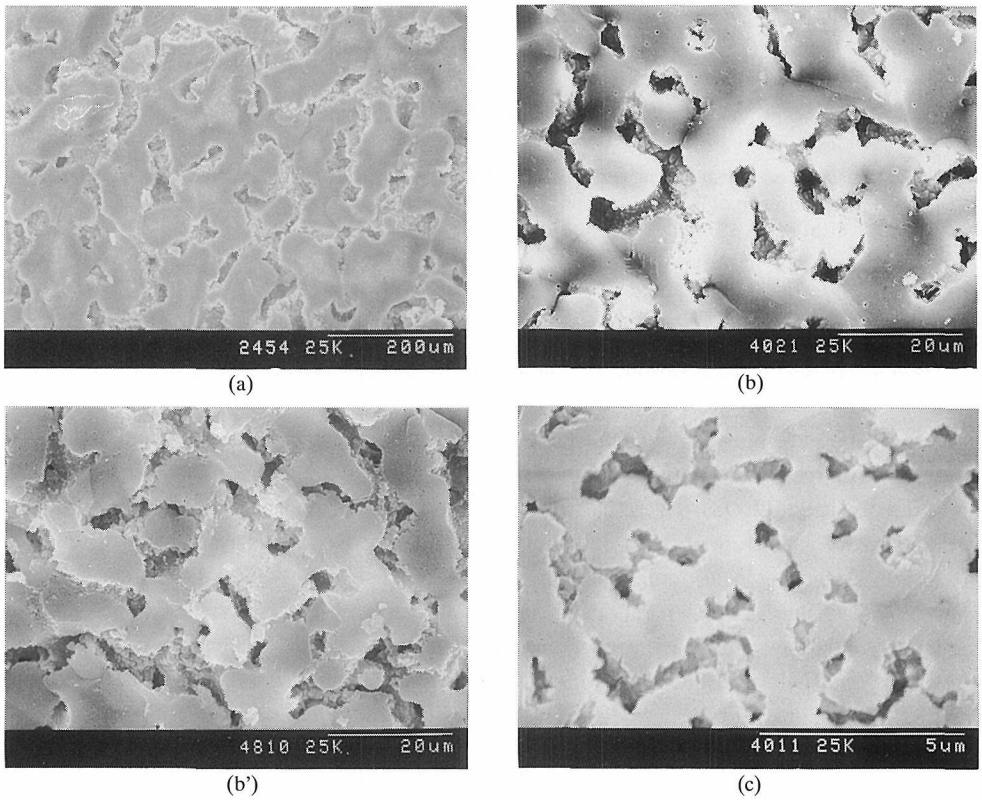
Sample	T (°C)	TBOT (g)	m[b] (%)	BuOH (g)	t_g (min)
S25-40	40	none	0	0.795[c]	135[d]
S25-60	60	none	0	0.795[c]	40
ST25-(a)	40	0.798	3.76	none	115
ST25-(d)	40	0.913	4.31	none	110

a): The amount of PA25 was fixed at 0.40g (C = 0.093). Components not specified in this table are the same as shown in table 1.

b): The amount of TBOT is expressed by m, mole fraction (%) against sum of TMOS and TBOT; $m = 100 \cdot n_{TBOT}/(n_{TMOS}+n_{TBOT})$, where n's denote respective mole amounts.

c): BuOH was added in order to adjust the solvent composition almost equal to that of ST25-(d) assuming complete hydrolysis of TBOT.

d): As this sample underwent phase separation before homogeneous gelation, the moment when the sediment layer lost its fluidity was recorded as t_g.



(a) (b) (b') (c)

Fig. 2. SEM photographs of dried gels prepared from PA25-TMOS-TBOT (ST25) system. The amount of HPAA is expressed by C, molar ratio of monomeric unit of HPAA to TMOS[4]. (a): m=3.76, C=0.093, (b): m=4.00, C=0.093, (b'): m=4.00, C=0.111, (c): m=4.15, C=0.093.

ples were almost transparent at the moment of gelation and gradually became turbid. The resultant morphologies were interconnected structures with their domain size steeply decreasing with TBOT concentration as shown in fig. 2. The pore size distribution curves of the samples corresponding to (b) and (c) in fig. 2 are presented in fig. 3. Both gels exhibit sharply distributed micrometer-range pores together with those in nanometer-range. At the TBOT concentration of m=4.31, the dried gel retained only nanometer-range pores.

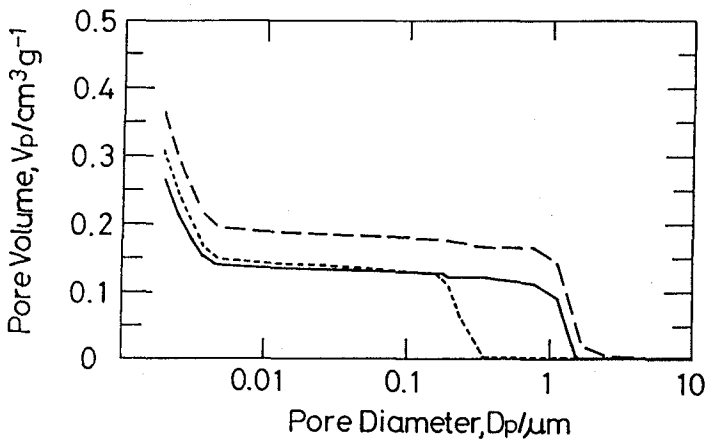


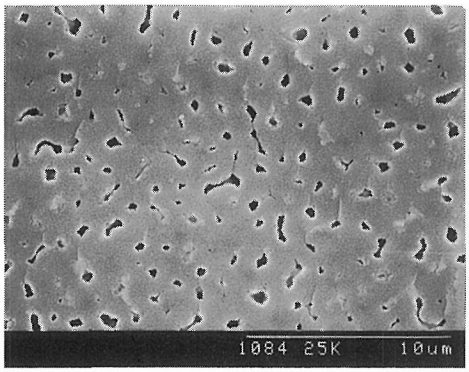
Fig. 3. Pore size distribution curves of heat-treated (600°C 2h) gels determined by mercury porosimetry (D_p>10 nm) and nitrogen adsorption method (D_p>10 nm). Solid line: (b) of fig. 2, broken line: (b'), dotted line: (c).

(3) Effect of HPAA concentration

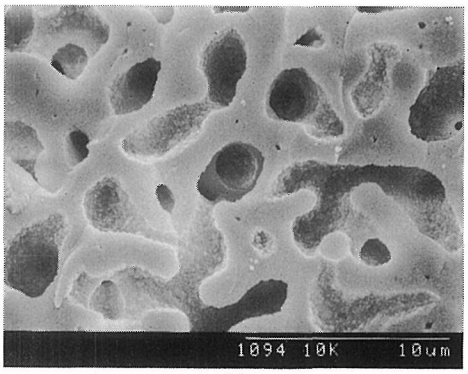
When HPAA concentration, C, increased in PA25 system at the fixed amount of TBOT, m, the overall morphology varied little (fig. 2(b) and (b')). Mercury porosimetry measurements gave almost the same micrometer-range pore sizes but somewhat larger pore volume with larger value of C (fig. 3). This result is in good agreement with that of PA25-tetraethoxysilane (TEOS) system[9], which showed almost constant domain size against varied PA25 concentration. For the samples containing PA1, the obtained morphologies are shown as fig. 4. The domain size increased with increasing value of C under the fixed value of m. It has also been reported that the gels in PA1-TEOS system exhibit a similar tendency[9]. These similarities of dependence of domain size on concentrations of PA25 and PA1 suggest that, in SiO_2-TiO_2 and SiO_2 systems, the roles of HPAA in the gel-formation and phase separation processes are not quite different from each other[4,9].

(4) Role of titanium alkoxide

The composition analysis of heat-treated (600°C, 2h) gels revealed that about half amount of initially mixed titanium was remaining in the oxide network. As the syneresis liquids of samples containing TBOT were slightly yellowish, the other half might be colloidally dispersed in a strongly acidic solvent phase. It is well known that the hydrolysis



(a)



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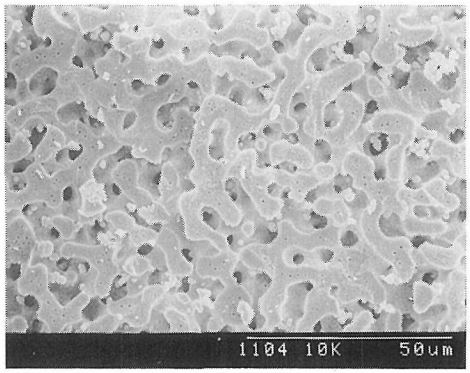
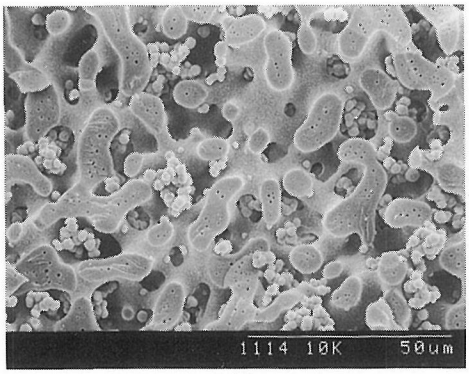
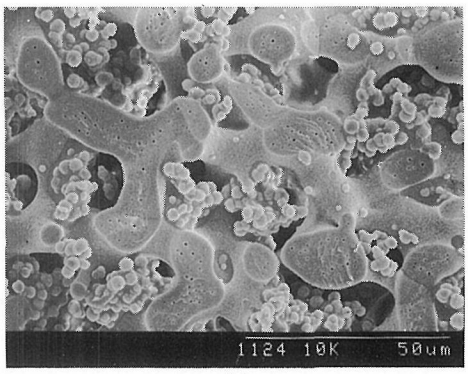


(c)



(d)



(e)

Fig. 4. SEM photographs of dried gels prepared from PA1-TMOS-TBOT (ST1) system. C
(a) 0.328, (b) 0.369, (c) 0.410, (d) 0.451, (e) 0.493.

and polycondensation kinetics of TBOT are faster than those of TMOS by several orders of magnitude[10], and that titanium alkoxide catalyzes silanol condensation under acidic and water-poor conditions[11,12]. However, the effect of titanium alkoxides incorporated in silanol condensations under a water-rich condition is known little.

As described above, the domain size of TMOS-TBOT gels steeply decreased with TBOT concentration accompanying only a slight decrease in gelation time. Even with much faster gel formation, TMOS gel at 60°C gave domains quite coarser than those of TMOS-TBOT ones. This effect of TBOT resembles that of additional good solvent of HPAA in PA25-TEOS system[13]. The good solvent works to lessen the segregation tendency between HPAA and SiO_2 gel, thus retards the occurrence of phase separation relative to the sol-gel transition. The retarded phase separation is far more effective than accelerated gelation to give fine domains[13]. The gradual progress of phase separation within a loosely cross-linked gel phase was commonly observed in TMOS-TBOT and PA25-TEOS-good solvent systems. In the present case, however, since the solvent compositions are almost the same in TMOS and TMOS-TBOT systems, the difference should be attributed to the nature of the oxide gel network.

The rapid gelation and subsequent slow consolidation are general trends of base-catalyzed alkoxy-derived SiO_2 condensations[10]. Under water-rich conditions, the preferential condensation reactions between highly condensed species result in a broad or bimodal distribution of molecular weight, allowing the sol-gel transition to occur by a percolation among a small fraction of exceptionally large sized polymers. On the other hand, silanol condensations under highly acidic and water-rich conditions produce loosely cross-linked species with relatively narrow size distribution, and, in this case, the sol-gel transition occurs after a substantial number of bridging bonds are formed. The latter condensation process is based on a higher condensation probability of silanol groups situated on monomers or weakly branched oligomers than those on highly condensed ones. If the condensation probability of silanol groups on highly condensed species are increased by the coexistence and incorporation of titanium alkoxide similarly to the case under water-poor conditions, the whole condensation process would shift to that of base-catalyzed case. This modification of the condensation process leads to the decreased cross-link density at the sol-gel transition, resulting in the later occurrence of phase separation. In order to confirm this hypothesis on the role of titanium alkoxide, more direct evidences are required of the variation in the gel formation process, e.g. mechanical or viscosity measurements of gelling samples.

(5) Extension of composition range

A further extension of the present process to higher titanium concentration will necessarily be linked with an improvement of the molecular level homogeneity. Among several alternative methods, the use of precursors containing Si-O-Ti bond would be the most direct way[10], and chemical modifications of alkoxides are also realistic. In addition, non-carboxyl polymers with considerable solubility in water and alcohols, such as polyethylene oxide, have to be used to avoid strong specific interaction between titanium and carboxyl groups. On the incorporation of polyethylene oxide, the results will be reported elsewhere[14].

CONCLUSION

SiO_2-TiO_2 gels with controlled macropores were prepared with additions of TBOT to the polymer-incorporated sol-gel reaction of TMOS by the co-hydrolysis method. About half amount of the initially added titanium could be incorporated in the gel network. The resultant domain size of gels decreased steeply with the TBOT concentration. The main role of TBOT was considered to modify the polycondensation mechanism of silica and make it analogous to that of base-catalyzed system, which can retard the occurrence of phase separation relative to the sol-gel transition.

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